

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No: 10/537,651
Applicant: Lindall *et al.*
Filed: October 31, 2005
Title: CATALYST AND PROCESS
T.C./A.U.: 1793
Examiner: McDonough, James E.
Confirmation No.: 5162
Docket No.: JMYS-128US

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF RICHARD WARD, Ph.D. PURSUANT TO 37 CFR §1.132

I, Richard Ward, Ph.D., being duly warned that willful false statements and the like are punishable by fine or imprisonment or both, under 18 U.S.C. §1001, and may jeopardize the validity of the patent application or any patent issuing thereon, state and declare as follows:

1. All statements herein made of my knowledge are true and statements made on information and belief are believed to be true.
2. I received my Ph.D. in Chemistry at the University of Durham in 2006. I received my Masters of Chemistry from the same university, in 2003.
3. I have been employed by Johnson Matthey PLC for 3 years, of which 15 months have been spent in the VERTEC™ business unit. I am currently the Technical Development Manager and am responsible for the polymers research and development team, which includes ensuring the effective polyurethane catalyst product platform development and commercialization and running the technical support and product development for the polyester products. A copy of my *curriculum vitae* is attached hereto.

4. I have read, and am familiar with, the contents of this patent application, the Office Action dated August 3, 2009, and the cited reference, European Patent No. 0 812 818 (Ridland et al.). I understand the nature of the obviousness rejections at issue in this application. In particular, the Office has asserted that the amount of base as claimed would have been obvious at the time of this invention based on routine experimentation absent any evidence of unexpected results or criticality of the claimed range. This declaration addresses these issues.
5. The experiments discussed herein were conducted under my supervision.
6. As shown in the described experiments, the molar ratio of base to acid is critical because, when the composition includes 1,4-butane diol, at base to acid ratios at 0.8 or higher formed an undesirable viscous gel, which was unsuitable for use as a catalyst. On the contrary, catalyst compositions with a molar ratio of base to acid in the range of 0.01 - 0.6:1 surprisingly formed a clear mobile liquid suitable for use as a catalyst, for example, in polyester-forming processes. As described below, polyesters made using the catalyst according to the invention, in the claimed base to acid range of 0.01 - 0.6:1, exhibited a lower T_g (glass transition temperature) and a significantly higher T_h (crystallization temperature) than polyesters prepared from a catalyst outside the claimed range. This is significant because the higher crystallization temperature allows for a wider range of temperatures during melt processing, which is above the T_g and below the T_h , before the polyester structure sets during crystallization.
7. Composition "A" was prepared using 1,4-butane diol as follows. Anhydrous citric acid (274.3 g, 1.43 moles) was dissolved in warm, deionised water (209.0 g) in a one-litre fishbowl flask fitted with a mechanical stirrer, condenser and thermometer. Titanium isopropoxide (VERTEC™ TIPT) (162.2 g, 0.57 moles) was added slowly from a dropping funnel, which resulted in the formation of a white suspension. Once the addition was complete, an azeotrope of isopropanol and water (81.1 g) was removed by distillation (86°C), which resulted in a slightly hazy, pale yellow/green solution. The stirred product was then allowed to cool to 49°C and aqueous sodium hydroxide (32 wt.%, 142.7 g, 1.14 moles) was added slowly from a

dropping funnel. The resulting product was allowed to cool (31.0°C) and then mixed with 1,4-butane diol (411.1 g, 4.56 moles), which resulted in a white suspension. The product was then heated to remove an azeotrope of isopropanol and water (92.6 g) by distillation (100 °C), which resulted in a slightly hazy, pale yellow/green solution. Once cooled to room temperature the product ("A") was an opaque, viscous, yellow/green liquid. On standing overnight, the viscosity of the mixture increased and formed a viscous white gel.

8. The mole ratio of citric acid : titanium : sodium hydroxide : butane diol used in the above preparation is 1.43 : 0.57 : 1.14 : 4.56. This composition is compared with the examples in the patent application in the Table below. Rows 1 to 5 are copied directly from the patent application. Row 1 is a comparative example of a composition prepared according to the method of Example 5 of the Ridland reference, using the same reactants in the same proportions, except for the substitution of 1,4-butane diol for the ethylene glycol used in Ridland. Composition 1 also formed a gel.

Example	Titanate	Base	mols base mols acid	Diol	mols diol mols Ti
1*	TIPT	NaOH	1.20	1,4-butane diol	8
2	TNBT	NaOH	0.53	1,4-butane diol	8
3	TNBT	NaOH	0.34	1,4-butane diol	8
4	TNBT	NaOH	0.35	1,4-butane diol	12.4
5	TIPT	NaOH	0.35	1,4-butane diol	8.1
A*	TIPT	NaOH	0.8	1,4-butane diol	8

Table 1 (* indicates Examples outside of the claimed range)

9. The composition made in the experiment described above is shown as "A" in the Table. As described above, this composition also formed a viscous gel and would be unsuitable for use as a catalyst composition in the preferred polyester-forming processes. There is, therefore, a significant difference between the compositions made using the minimum amount of base taught by Ridland and the compositions claimed in the present application, which use 0.6 moles of base (or less) per mole of acid.

10. The preparation and thermal analysis of PET polyester was conducted as follows. Two catalyst compositions were prepared according to the method described generally in Example 14 of the present application. Composition B was made using 0.8 moles of sodium hydroxide per mole of citric acid. Composition C was made using 0.4 moles of sodium hydroxide per mole of citric acid.
11. A batch of polyethylene terephthalate (PET) was prepared using each of the catalyst compositions B and C. A standard method of preparation was used which was the same for each batch, apart from the composition of the catalyst. Samples of the PET were investigated using DSC thermal analysis methods, following the procedure described on page 12 at lines 19 – 24 of the present application. The results are shown in Table 2 below.

PET sample	mols base mols acid in catalyst	T _g (°C)	T _n (°C)	T _n (°C)	ΔH (J/g)	T _p (°C)	ΔH (J/g)
B	0.8 .	81	149	159	-21	254	27
C	0.4 .	71	150	171	-26	253	25

Table 2

12. PET sample C, in the claimed range of 0.01 - 0.6:1, has a lower T_g (glass transition temperature) and a significantly higher T_n (crystallization temperature) than PET sample B, outside the claimed range, which is made using the catalyst having a composition in which the mole ratio of base : acid is 0.8. As previously explained in the present application and also in paragraph 13 of the Declaration of Calum Harry McIntosh dated 28th May 2009, the higher crystallization temperature of PET sample C provides a benefit when the PET is melt processed and oriented or drawn into articles such as bottles, films or fibres. Namely, the benefit is that the orientation can take place between a wider range of temperatures above the T_g and below the T_n before the PET structure sets on crystallization.



22/12/09.

Richard Ward, Ph.D.

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Office Action of August 3, 2009

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Date:

Attachment: Curriculum Vitae

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Employment and Education History

2008-Present: Technical Development Manager, Johnson Matthey Catalysts

Working for the VERTECT™ business unit of Johnson Matthey Catalysts I manage the polymers research and development team. I am responsible for ensuring the effective polyurethane catalyst product platform development and commercialisation and also for running the technical support and product development for the VERTEC AC product range for polyester applications. Both product ranges have a strong heavy metal catalyst replacement focus. My responsibilities in the PET area have involved the testing and technical service work for our titanium based catalyst products with regard to antimony catalyst replacement in tradition PET systems. Comparison between Sb and Ti catalysis in a range of PET applications, including film, fibre and resin applications is a key area of work.

2006-2008: Research Scientist, Johnson Matthey Technology Centre

I carried out research on a number of catalyst projects particularly in the areas of tin-free homogeneous catalysts for polylactic acid and silicone sealant applications and 'CoMo' type heterogeneous catalysts for sulfur removal in liquid hydrocarbon streams.

2003-2006: Ph.D in Chemistry, University of Durham

Working for Prof. Todd Marder I investigated a novel luminescent rhodium based organometallic system. This involved organic and air-sensitive chemistry techniques as well as analytical measurements on the photo-physical properties of the material. Seven publications were made on this work during this time and the research is still ongoing in the Marder group.

1999-2003: Chemistry degree (M.Chem.), University of Durham

M.Chem. - 1st class (Hons)